US Army Corps of Engineers ®

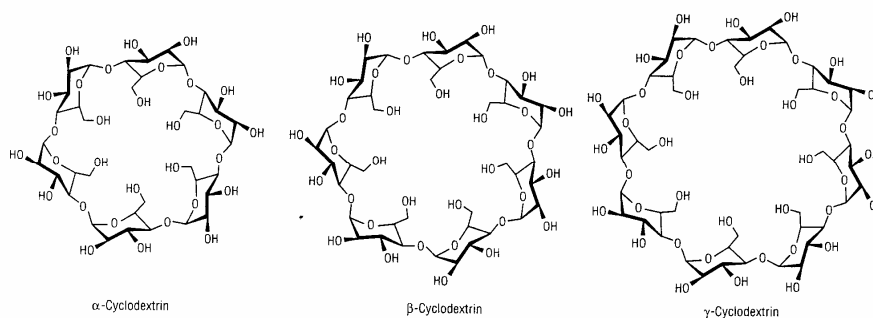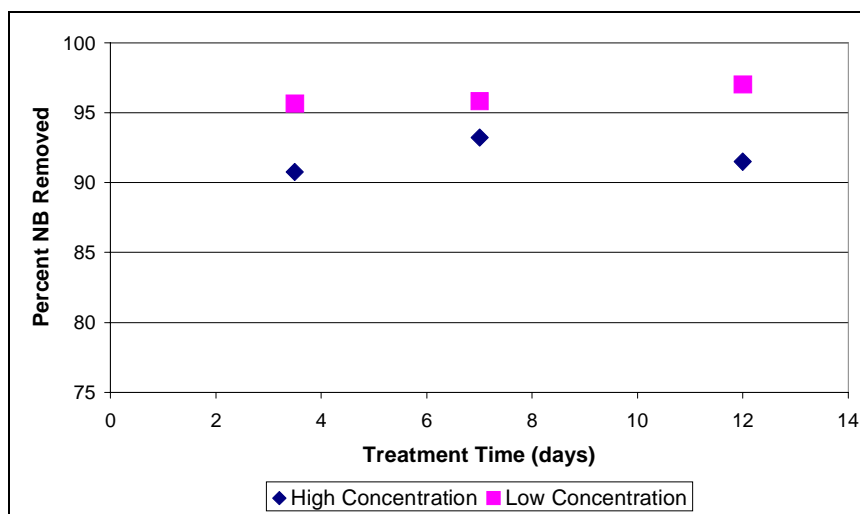Engineer Research and Development Center

Investigation of Cyclodextrin-Enhanced Electrokinetic Soil Remediation

Fate and Transport of Nitroaromatic Contaminants and Cyclodextrin Amendments in Expansive Clays

David Kessler, Charles P. Marsh, John J. McCormick, Donald M. Cropek, Angelo R. Deguzman, Ruben Robles, and David Gent

September 2004

α-Cyclodextrin   β-Cyclodextrin   γ-Cyclodextrin

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Final Report

ABSTRACT: Nitroaromatic-based compounds can pose a serious threat to ecosystems and human health. These compounds, which have been used in munitions and pesticides, are present in soil and groundwater at military installations and other sites. The presence of these contaminants in clayey soils poses a difficult and potentially costly remediation problem. The low hydraulic conductivity of these soils prohibits the use of conventional pump-and-treat remediation techniques, and high energy costs make the process of excavating and thermally treating the soil highly inefficient and damaging to the environment. For these reasons, much research has been done to advance the field of electrokinetic remediation as a viable cleanup technique. Although some studies have reported that organic molecules can be removed from clayey soils by electro-osmosis alone using a purging solution, the addition of amendments to the solution has increased removal efficiencies.

The objective of this research was to advance the state of knowledge on a novel technique for cost-effective remediation of nitroaromatic compounds using cyclodextrin molecules as solubilizing agents and electrokinetically transports them through the contaminated zone. The results provided direct evidence that it is possible to remove nitrobenzene and 2,4-DNT from expansive montmorillonite clay using electro-osmosis both with and without cyclodextrin amendments.

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Conversion Factors

U.S. standard units of measure can be converted to SI[*] units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic feet	0.02831685	cubic meters
cubic inches	0.00001638706	cubic meters
degrees (angle)	0.01745329	radians
degrees Fahrenheit	(5/9) x (°F – 32)	degrees Celsius
degrees Fahrenheit	(5/9) x (°F – 32) + 273.15.	kelvins
feet	0.3048	meters
gallons (U.S. liquid)	0.003785412	cubic meters
horsepower (550 ft-lb force per second)	745.6999	watts
inches	0.0254	meters
kips per square foot	47.88026	kilopascals
kips per square inch	6.894757	megapascals
miles (U.S. statute)	1.609347	kilometers
pounds (force)	4.448222	newtons
pounds (force) per square inch	0.006894757	megapascals
pounds (mass)	0.4535924	kilograms
square feet	0.09290304	square meters
square miles	2,589,998	square meters
tons (force)	8,896.443	newtons
tons (2,000 pounds, mass)	907.1847	kilograms
yards	0.9144	meters

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[*] SI: *Système International d'Unités* (International System of Measurement).

Preface

1 Introduction

Background

It is well known that nitroaromatic compounds can pose a serious threat to eco-systems and human health. These compounds have been used for many years in military munitions and pesticides, and they are present in high concentrations below ground at various sites across the country. This problem is of particular interest to the U.S. Army because it has operated munitions manufacturing facilities on many of its installations. There are hundreds of explosives-contaminated sites around the United States related to Army activities. More than 100 sites are listed in the Defense Site Environmental Restoration Site Tracking System as having groundwater and, by logical extension, soils contaminated with explosives. These sites have the potential to adversely affect drinking water aquifers, creating the likelihood of regulatory compliance problems. The U.S. Environmental Protection Agency (EPA) recognizes that explosives-contaminated drinking water is a problem, and future EPA regulatory limits on nitroaromatic compounds in the water supply could seriously impair the military mission by restricting the breadth and scope of the munitions manufacturing program as well as Army training activities in the field. Consequently, the Army has a high interest in the development of cost-effective techniques for remediation of soil contaminated with nitroaromatic compounds.

It has been proposed by many authors that natural organic material in soil acts as the primary sorbent for organic compounds such as nitroaromatics (16, 17, 31). Other studies have shown that, in certain situations, the clay mineral phase can dominate the adsorption process (20, 36). But owing to the relative difficulty encountered when attempting to decontaminate clay minerals, it is the latter of those two sorption mechanisms that is of primary concern to the present study. Haderlein et al. (12) have calculated adsorption coefficient (K_d) values for various substituted nitrobenzenes (SNBs) and found that many of these compounds form very strong adsorption complexes with several types of clay minerals. These authors also report increasing adsorption capacity depending on the specific clay type, in the order kaolinite < illite < montmorillonite (11). This finding suggests that soils composed primarily of montmorillonite would be the most difficult to treat due in large part to the swelling properties of this clay type. If that were

true it would be a major concern because a large portion of the United States consists of soils with some fraction of clays that have high to medium swelling potential (Figure 1).

MAP LEGEND

🟥	Unit contains abundant clay having high swelling potential
🟦	Part of unit (generally less than 50%) consists of clay having high swelling potential
🟧	Unit contains abundant clay having slight to moderate swelling potential
🟩	Part of unit (generally less than 50%) consists of clay having slight to moderate swelling potential
🟫	Unit contains little or no swelling clay
🟨	Data insufficient to indicate clay content of unit and/or swelling potential of clay (Shown in western most states only)

Figure 1. Map of predominant clay types throughout the United States.

The presence of contaminants in clayey soils poses a difficult and potentially costly remediation problem. The low hydraulic conductivity of these soils prohibits the use of traditional pump-and-treat remediation techniques, and high energy costs render the process of excavating and thermally treating the soil highly inefficient and damaging to the environment. For these reasons, much research has been done to advance the field of electrokinetic remediation as a viable cleanup technique. Most of the research performed to date has focused on the removal of heavy metal contaminants through coupled electro-osmosis and electromigration of the ionic contaminants (1, 3, 14, 21, 26, 32 – 34, 41) although some studies have been performed detailing the removal of organic molecules by electro-osmosis alone (18, 19, 27, 37, 38). The interested reader is referred to a more complete review of the aforementioned research and the state of the art of

electrokinetic remediation recently published by M. M. Page and C. L. Page (25). Adding amendments to the purging solution has increased removal efficiencies of organic molecules. For instance, Shapiro and Probstein showed that the removal of phenol from kaolinite was enhanced by adding an alkaline purge solution (37), and Ko et al. used hydroxypropyl-β-cyclodextrin in solution to enhance the solubility of phenanthrene and thus facilitate its removal from kaolinite (18). It should be noted that most of these studies were performed on non-expansive clays and do not address the difficulty encountered with an expansive clay type.

Cyclodextrin (CD) molecules have the ability to form complexes with many different molecules. In particular, Cahill and Bulusu showed that RDX and HMX, common nitroaromatic molecules, form complexes with γ-CD while TNAZ prefers to complex with β-CD (5).* Hawari et al. showed that the addition of CDs enhanced recovery of RDX from artificially contaminated illite and organic-rich topsoil in batch experiments (13). Later, Sheremata and Hawari reproduced the above result using 2,4,6-trinitrotoluene (39). Perez-Martinez et al. demonstrated enhanced removal of the herbicide 2,4-dicholorophenoxyacetic acid from a Spanish soil composed mainly of iron oxides using β-CD in a batch study (29).

Objective

The objective of this research was to advance the state of knowledge on a novel technique for cost-effective remediation of nitroaromatic compounds that uses cyclodextrin molecules as solubilizing agents, and transports them through the contaminated zone using an electrokinetic (EK) process.

Approach

First, a thorough review of the relevant literature was performed. Based on the findings of the review and the authors' previous experience in this technical domain, an EK test cell was designed and fabricated. Preliminary testing of EK performance through uncontaminated soil without the addition of CD was performed to gain insight into the values of enhanced operating parameters. Concurrently, a thorough chemical study of the physical behavior of CDs in the pres-

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*   RDX is Royal Dutch Explosive; HMX is High-Melting Explosive; TNAZ is trinitroazetidine.

ence of contaminants and clay particles was performed by the ERDC-CERL Environmental Chemistry Laboratory. Upon completion of the preliminary experiments, testing was conducted to determine the ability of electro-osmotic flow to transport CDs through a clay column. Finally, an experimental study was performed to determine whether CDs in combination with an electrokinetic process can remove model contaminants from a clay column. Specific issues investigated included the following:

1. The ability of electrokinetics to successfully transport CDs, CD/contaminant association complexes, and contaminants alone through expansive clay.
2. The ability of CD molecules and an electrokinetic process to desorb model contaminants from expansive clay.
3. A CD/contaminant complex detection method using x-ray diffraction.
4. The stability of the CD molecule under the influence of an electric field.

Mode of Technology Transfer

The findings of this study will be disseminated to the research community through publication in a journal of environmental engineering or applied chemistry. The results are appropriate and suitable for transition into an Army-sponsored Research, Development, Test, and Evaluation (RDTE) 6.2 advanced development project.

2 Technical Foundations

Review of Electrokinetic Theory

Double Layer Theory

A first attempt at explaining the recently observed electrokinetic phenomena was put forth by Helmholtz (6) describing what is now known as the "electric double layer." In his model, the net positive charge at the solid surface attracted a rigidly held parallel layer of negative ions. This layer of negative charges was fixed to the solid surface via coulombic forces. Just beyond this layer of negative charges, at a molecular distance from the wall, existed another layer of positive charges. Helmholtz proceeded to express the potential drop, ΔV, across this double layer by treating it as a parallel plate capacitor as given in Equation 1:

$$\Delta V = \frac{4\pi e d}{D} \qquad (1)$$

Where e denotes the charge density in the double layer, D is the dielectric constant of the solution, and d is the distance across the double layer. This simple model had several shortcomings that were subsequently resolved by the "diffuse double layer" model proposed by Gouy (50). In this model, the fixed inner layer was allowed to have a net negative charge, beyond which an excess of positive ions were available in free solution to balance the charge. These positive ions were not bound to the solid surface and were free to move under the influence of an electric field. The difference in potential between the interface of the fixed and mobile layers and the bulk fluid is termed the zeta potential, ζ, and describes the capacity of the solution to sustain electro-osmosis.

Electro-Osmotic Flow

The first attempt at extending the double layer theory to describing electro-osmotic flow was given by Smoluchowski. He considered the flow through a narrow cylindrical capillary tube with net positive wall charge. Making several assumptions as to the nature of the flow field along with the assumption that the

diameter of the capillary was large compared with the size of the double layer, he arrived at the following well known expression describing the volumetric flow rate:

$$q_e = \frac{D\zeta aE}{4\pi vL} \quad (2)$$

where a is the cross-sectional area of the capillary, E is the magnitude of the applied electric field, L is the length of the capillary, and υ is the kinematic viscosity of the fluid. It is simple to extend this theory to describe the flow rate through a porous medium by modeling the medium as a collection of independent parallel capillaries filling the open space of the medium. This introduces a factor known as porosity, n, to describe the fraction of the medium that is blocked by solid material. The total flow rate through the porous medium would then be given by

$$Q_e = \frac{nD\zeta AE}{4\pi vL} = k_e \frac{E}{L} A \quad (3)$$

where A denotes the total cross-sectional area of the porous medium and k_e is an engineering parameter known as the electro-osmotic permeability. Equation 3 is only a very crude approximation to the real flow situation within a porous medium, but can be useful in large-scale engineering calculations.

It is not the intent of the current discussion to present any new advances in the analytical modeling of electro-osmotic flows, but the full governing differential equations for the treatment of electro-osmosis at the pore-scale will be presented for completeness. The three measurable quantities of interest are the spatial and temporal fluid velocity field $\mathbf{u}(\mathbf{r},t)$, concentration of ionic species $n_i(\mathbf{r},t)$, and electrical potential $\psi(\mathbf{r},t)$.[*] In a porous medium characterized by small-scale pores, the Reynolds number of the flow will always be much less than unity. This means that the fluid velocity field can be modeled using the unsteady Stokes equations given in Equation 4a below, which are derived from the full Navier-Stokes equations in the limit of vanishing Reynolds number. The rele-

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[*] The bold-face characters in this expression indicate a vector quantity.

vant physical parameters in this equation include the dynamic viscosity μ and the fluid density ρ_f. The body force term $\mathbf{f}$ is modeled by the relationship given in 4b. In this formulation, gravity is neglected in favor of an electric force density. Note that e denotes the electron charge, n_i and z_i denote the concentration and valence of the ith ionic species, respectively, and $\rho(\mathbf{r},t)$ denotes the electric charge density. The electric potential field is governed by the Poisson equation given in 4c where ε is used to denote the dielectric constant of the solution. The final relations needed to close the system of equations are given in 4d and 4e where $\mathbf{j}_i$ denotes the flux of the ith chemical species, D_i is the ion's diffusivity, and b_i is the ion's electric mobility.

$$\rho_f \frac{\partial \mathbf{u}}{\partial t} = -\nabla p + \mu \nabla^2 \mathbf{u} + \mathbf{f}, \qquad \nabla \cdot \mathbf{u} = 0 \qquad (4a)$$

$$\mathbf{f} = \sum_i e n_i z_i \nabla \psi = \rho \nabla \psi \qquad (4b)$$

$$\nabla^2 \psi = -\frac{\rho}{\varepsilon} \qquad (4c)$$

$$\frac{\partial n_i}{\partial t} + \nabla \cdot \mathbf{j}_i = 0 \qquad (4d)$$

$$\mathbf{j}_i = -D_i \nabla n_i - e z_i b_i n_i \nabla \psi + n_i \mathbf{u} \qquad (4e)$$

Equations 4a – 4e completely describe the physics occurring within a narrow pore volume. However, difficulties still exist in scaling this continuum approach to the next level of complexity to describe flow through a porous medium owing to the extreme complexity of the resulting boundary conditions. Recent work by Adler, Berki, and Thovert (2) has advanced the frontiers of this subject, but the current state of the art is far from adequate to model the complex physics associated with decontamination of porous media. It is unclear as to whether a significant modeling advantage over that of the Smoluchowski model will be realized by including all of the physics given in Equation 4. More research is required in this arena to give a definitive answer.

Cyclodextrin Chemistry

Cyclodextrins (CDs) are of widespread interest to the research community because of their ability to capture molecules as a part of host-guest interactions. They are produced in large quantities using environmentally friendly technologies for the enzymatic conversion of starch. They also are currently utilized in many commercial applications and analytical methods (42). Applications include pharmaceuticals, cosmetics and fragrances, chromatography, food processing, flavoring, textile processing, paint processing, catalysis, and enzymatic models (15).

Villiers discovered CDs in 1891 by digesting starch with Bacillus amylobacter and Bacillus macerans spores (42, 46). The structures of CDs have been determined (42) and are reproduced in Figure 2. They can be described as crystalline, homogeneous, nonhygroscopic substances forming torus-like rings built up from glucopyranose units. The three major cyclodextrins (α-CD, β-CD and γ-CD) are constructed of six, seven, and eight glucopyranose units, respectively. The CD ring is a conical cylinder with secondary hydroxyl groups situated on one edge of the ring and primary hydroxyls situated on the other edge. The cavity is lined by hydrogen atoms and glycosidic oxygen bridges. Thus, cyclodextrins exhibit hydrophilic nature on the outside of the rings and hydrophobic characteristics inside the cavity. The cavities are approximately 8Å deep and range in diameter from 5—10 Å depending on the specific CD, so they can therefore accommodate different sized organic guest molecules. The hydrophilic exterior provides water solubility for the CD while the hydrophobic interior provides an energetically favorable site for adsorption of organic contaminants to create a water soluble inclusion complex. Hydrogen bonding, electrostatic forces, and van der Waals forces all serve to attract and hold organic molecules in the CD cavity (24).
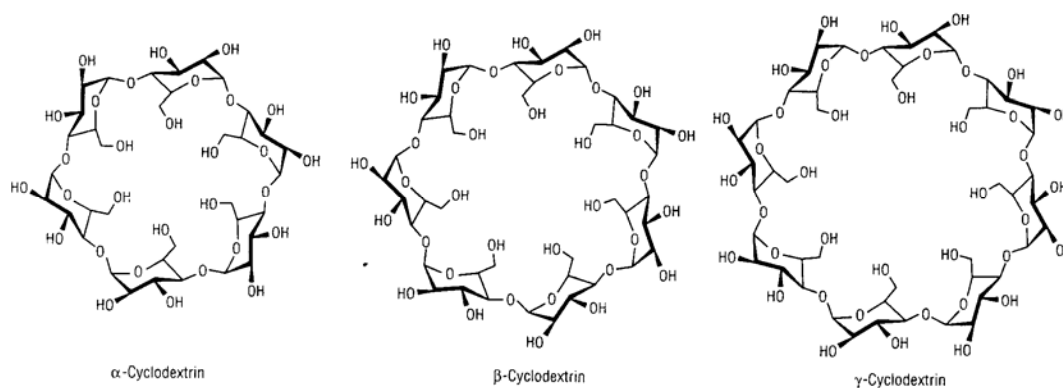
Figure 2. Chemical structures of the native cyclodextrin molecules.

An attractive feature of CD molecules is the availability of numerous hydroxyl (OH) groups for chemical modification. The total number of OH groups on each CD molecule, both exterior and interior, is considerable and varies with the size of the specific CD (α-CD =18, β-CD = 21, γ-CD =24). Thus the number of possible derivatives is nearly limitless (42). Examples of replacement of the OH group with the following functional groups have been reported: iodide, azide, thioacetate, hydroxylamine, alkyl, polyalkylamines (24), monoiodo (45), azido (22, 44), thio (10, 40), hydroxylamino (9), and alkylamino cyclodextrins (30, 43). The chemistry of modification is well characterized, including selective modification at specific sites on the molecule, so one can assemble 'customized' CD molecules suitable for a specific application. Also, both anionic CDs and cationic CDs have been synthesized (7). In addition, modified CDs exhibit enhanced complexing properties and solubility compared with the unmodified forms. (The incremental resources needed to investigate various modified CDs as part of the current group of experiments was not available.)

Clay Physics

Clay-Contaminant Interaction Processes

In order to develop an electro-osmotic remediation technology that exploits the unique properties of CDs, it is important to understand the complex physical processes that take place to bind or remove an organic contaminant to the surface of a clay mineral. Considerable amounts of research have been performed in this area dating back to the 1960s. Mortland (23) listed several possible interactions that can take place between a clay mineral surface and an organic molecule. First, depending on the pH of the pore solution, an organic molecule can undergo protonation in which free hydrogen ions in solution bond with functional groups on the organic molecule to form a new organic molecule with a net positive charge. This molecule is then able to adsorb to the clay surface directly by exchanging with the other species of cation present on the clay surface. This effect becomes significant in clays with low water content and exchangeable cations with low hydration energies. A second process that commonly occurs is based on an electron-donor/electron-acceptor model. The exchangeable metal cations act as electron acceptors while the functional groups of the organic molecule become electron donors. This leads to an ion-dipole type interaction that indirectly binds the organic molecule to the clay. Metal ions with large hydration energies tend to retain a primary hydration shell, and the organic molecule then binds with this intermediate hydration shell via hydrogen bonding.

These results for the broad class of organic molecules were then specialized to nitroaromatic compounds by Haderlein et al. (12) and Boyd et al. (4). Haderlein et al. (12) champion the electron donor-acceptor hypothesis while Boyd et al. (4) refute that hypothesis and propose that electron-withdrawing groups (e.g., NO_2) engage in site-specific interactions with the exchangeable cations. Regardless of the mechanism, both studies concur that clays with exchangeable cations having low hydration energy can adsorb significantly more nitroaromatic compounds than those having high hydration energies. Also, the type of clay mineral determines the affinity of the compound for adsorption. As noted previously, the rank order of clay mineral types used in this study, from lowest adsorption capacity to greatest, is kaolinite, illite, and montmorillonite. Finally, there is a wide variation in adsorption constants among the different nitroaromatic compounds, with trinitrotoluene (TNT) adsorbing the most strongly to clay surfaces (12).

Implications of Crystalline Structure

Based on early optical microscopy studies, clays were thought to be amorphous hydrous gels consisting predominantly of silicon, aluminum, and iron. Then in 1923 Rinne and, separately, Hadding succeeded in obtaining x-ray diffraction patterns from what turned out to be the crystalline structure of clay minerals. The definitive publication is attributed to Pauling (28) who found a unit cell with dimensions in the plane of cleavage of approximately 0.50 x 0.88 nm that was common to micas, chlorites, pyrophyllite, talc, kaolinite, and gibbsite. As is now known, clays typically consist of layered crystalline structures in which sheets of octahedrally coordinated oxygen atoms centered on aluminum atoms are sequentially stacked, or are fused with tetrahedral coordinated layers based on silicon atoms. The varied and differing sequences of layering gives rise to specific types of clay. It should be noted that amorphous, small-diameter soil materials do exist (e.g., allophanes) but they are uncommon. These derive from very young rock such as lava flows, and will eventually alter in time to more conventional clay mineral crystalline structures. Thus, the behavior of the great majority of clay-containing soils is dominated by the layer lattice alumina-silicates. These materials are typically classed as 1:1 (a layer of tetrahedrally coordination around Si^{4+} bonded to an octahedrally coordinated layer around Al^{3+} or Mg^{2+}) and 2:1 (a basic layer unit of two tetrahedrally coordinated sheets forming a sandwich with an octahedrally coordinated sheet). The 1:1 layer silicates (e.g., kaolinite, halloysite, dickite, nacrite) are bonded to the next layer at a fixed basal spacing distance of 0.72 nm by hydrogen bonding and display no swelling behavior. The 2:1 layer silicates (e.g., montmorillonite, illite, pyrophyllite, talc, mica, vermiculite) can have fixed basal spacing (e.g., 1 nm for illite via non-exchangeable K^+) or can expand, often to a great degree. Montmorillonite, for example, begins with a

basal spacing of about 1.4 nm but can swell to many tens of nanometers into an expanded tactoid structure.

It is this variability in interlamellar spacing that is of interest and could be exploited to determine the nature and concentrations of the molecules present in solution. Rytwo et al. (35) have shown using x-ray diffraction techniques that the basal spacing of montmorillonite depends strongly on the type of molecule adsorbed and also on the concentration of this molecule. In addition, Dios-Cancela et al. (8) show that the basal spacings of montmorillonite clay to which a particular molecule has adsorbed depend on the exchangeable cation present on the clay surface. It is reasonable then to hypothesize that there exists a noticeable difference between the basal spacing when only a contaminant is present in the pore solution, when a CD molecule is present in the pore solution, and when a CD/contaminant complex is present in the pore solution. An exploratory x-ray diffraction experiment was conducted to test that hypothesis.

3   Experimental Procedure

Electro-Osmotic Test Cells and Expanded Procedure

Various expansive and non-expansive clays were mixed with water in the following soil-to-water ratios: montmorillonite 1:1, kaolinite 3:1, illite 5:1, and natural Champaign (IL) clay 3:1. The clay was rolled by hand into a ball and forced into columns. This process was performed carefully and slowly in order to minimize voids in the clay column. Twelve columns were packed with the appropriate type of clay and covered on each end with a 2 mm diameter thick rubber o-ring and a 1.7 mm diameter, 0.2 mm thick filter membrane. A covered column served as a conduit between two electrokinetic chambers. These elements were fastened together with threaded metal rods using 1.6 mm diameter washers and ¼ in. nuts. Engineering drawings of the apparatus are shown in Figure 3 and a photograph of the cells in use is shown in Figure 4.

A specially machined mixed-metal ceramic electrode was placed in each of the test cell reservoirs, one designated as the positive polarity anode chamber and the other as the negative polarity cathode chamber. A constant voltage was supplied to the test cells through a Kepco BOP100M power source controlled with Labview 5.1 computer software. Simultaneous current measurements through all 12 cells were taken at 60-minute intervals using a Keithley multimeter and recorded by LabView.

Liquid samples were drawn from the anode and cathode chambers of each cell at various intervals dependent on the particular experiment. The lost volume of liquid was then replaced with the appropriate background solution used in the particular experiment. (Further details of this procedure are provided in text with the results of each experiment.) The liquid samples were then analyzed for concentrations of the possible constituent molecules.
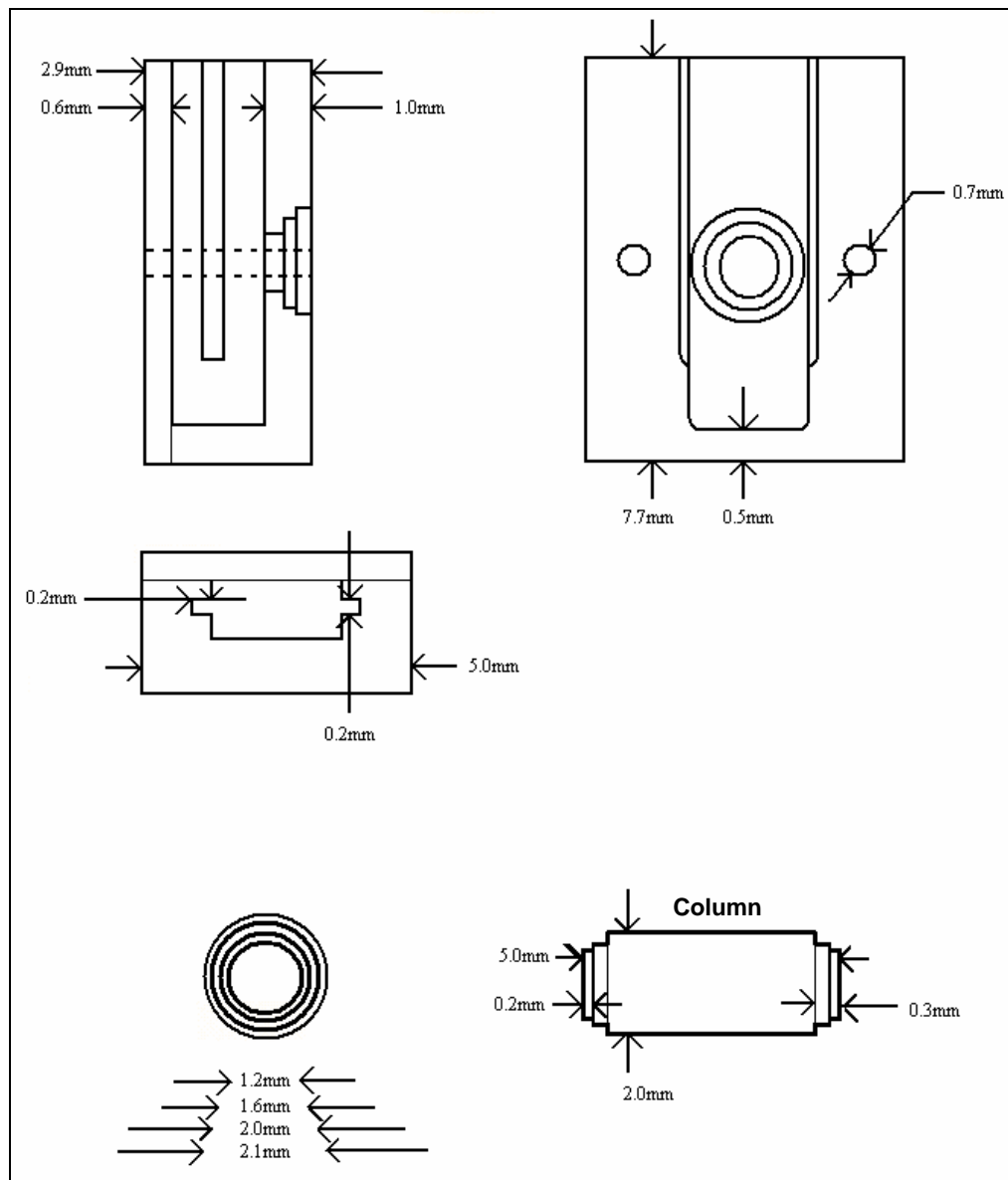
Figure 3. Engineering drawings of test cells.
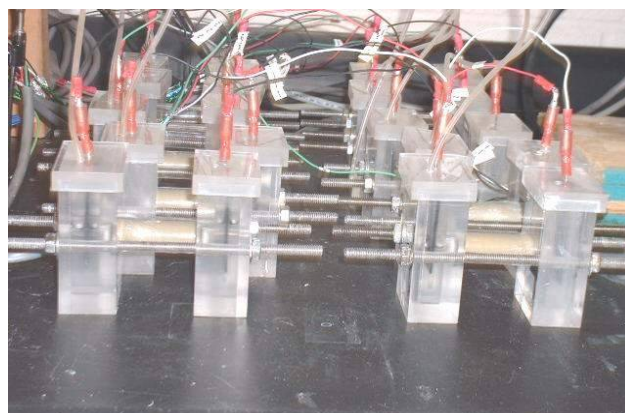
Figure 4. Photograph of test cells during operation.

Sample Analysis

Samples were filtered through Gelman GHP 0.2 μm filter membranes prior to analysis and then divided into two equal portions, one for nitroaromatic compound analysis and the other for CD analysis. A Waters Associates LC Module I system injected 10 μl samples through a Supelcosil ABZ+ Plus column (15 cm x 3 mm, 5 um particle size) to analyze the nitroaromatic compound content. An Eppendorf Column Heater held the temperature of the column constant at 35 °C. The Waters Model 486 UV/Visible absorbance detector detected the nitroaromatics at a wavelength of 254 nm. The mobile phase consisted of 70% deionized water / 30% acetonitrile flowing at 1 ml/min.

Two different high-performance liquid chromatography (HPLC) systems and columns were used to analyze the CD concentrations. The first system was used exclusively for detection of the native, α, ß, and γ-CDs. A Waters Associates LC Module I plus injected 40 μl samples into a Phenomenex Jupiter C18 column (250 x 4.6 mm, 5μm particle size, 300 Å pore size) maintained at 30.8 °C. A Wyatt Optilab Interferometric Refractometer was used to detect CD by changes in refractive index. For samples containing α and γ-CDs, the mobile phase consisted of 1.2% ACN / 98.8% deionized water. ß-CD required a 2.2% ACN / 97.8 % deionized water mobile phase to limit the analysis time to 20 minutes. The mobile phase flow rate was 1 ml/min.

A second system was required for detection of the modified ß-CDs (amino-, carboxymethyl-, hydroxypropyl-, maltosyl). A Waters Alliance HPLC system injected 20 μl samples containing these modified CDs into an Advanced Separations Technologies, Inc. (ASTEC) Cyclobond I 2000 column (250 x 4.6 mm) and maintained a constant 30 °C column temperature. The mobile phase, flowing at 1 ml/min, was 65% acetonitrile / 35% TEA buffer/water solution[*]. The TEA/water solution pH was adjusted to 4 by adding approximately 1—2 ml of glacial acetic acid. An Alltech ELSD (Evaporative Light Scattering Detector) 2000 detected the modified ß-CDs. The ELSD 2000 maintained the drift tube temperature at 100 °C, and set the nitrogen flow rate at 1.5 l/min.

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[*] 0.1% by mass triethylamine.

Soil Contamination

Various soils were artificially contaminated with 2,4-dinitrotoluene and nitrobenzene. Two 100 g portions of each soil were transferred to 500 ml wide-mouthed jars. To one of the jars was added 200 ml of a 2,4-DNT/ACN (10 g/L) solution. Similarly, 200 ml of an nitrobenzene/ACN (10 g/L) solution was added to the other. A total of 15 ml of water was added to all of the soil samples. These jars were then rotated for several days. After this time period, the jars were removed from the rotators and left to stand in an upright position for approximately 1 hour to allow the soils to settle. The remaining nitroaromatic/ACN solution above the settled soils was removed, and the soil slurries were then spread onto aluminum foil sheets under a fume hood and left to dry at room temperature for at least 4 days. The large pieces of soils that formed were crushed to finer particles using a mortar and pestle.

EPA Method 8330, *Determination of Concentration of Nitroaromatics and Nitramines by High Performance Liquid Chromatography* (49), was used to determine the concentration of nitroaromatic compounds in the soil. A 2 g sample of contaminated soil was mixed with 10 ml of ACN for 1 minute using a Vortex mixer. A Branson Ultrasonics Bath, maintained at 10 °C, sonicated the soil/ACN mixtures for at least 18 hours. After sonication, the samples were left to stand for at least 30 minutes to allow the soils to settle. Then, 5 ml samples of the solutions remaining above the settled soils were then transferred to another vial, and 5 ml of KCL solution (5 g KCL dissolved to 1 L mark with deionized water) were added to these and agitated. Again the samples were left to settle. Finally, 5 ml portions of these samples were filtered through Gelman 0.2um polytetra-fluoroethylene (PTFE) filter membranes, disposing of the first 3 ml and saving the last 2 ml for analysis in the Waters LC Module I system, as described above.

Electrostatic Degradation

Batch experiments were conducted to determine the degradation rate of various CDs and nitrobenzene in the presence of an electric field. A specified volume of CD or nitrobenzene in water was placed in a beaker, and two electrodes were suspended into the solution. A paraffin wrap was placed over the top of the beaker to minimize evaporation. A constant current was applied to the electrodes using a KEPCO BOP50M power supply controlled by LabView 5.1 software. The area of the front face of the immersed electrodes was measured. For the purposes of comparisons within this study, this area was assumed to be the effective cross-sectional area from which the current density was calculated.

Thus the effective current density between experiments was varied by changing the volume of liquid placed into the beaker.

Liquid samples were drawn periodically from the beaker and analyzed for CD or nitrobenzene content using the method described above under "Sample Analysis". The sample volume along with any evaporated liquid was replaced with deionized water after each sample was taken. Every effort was made to maintain the liquid at a constant level within the beaker to assure a constant current density throughout the course of the experiment.

X-Ray Diffraction

Eight montmorillonite and eight illite samples were prepared according to Table 1. A soil to cyclodextrin ratio of 1:1 was roughly followed to facilitate the detection of CD using the x-ray diffraction (XRD) technique. It should be noted that an exception to this was necessary for the amino β samples due to their limited availability. The amount of deionized water used in each sample was the minimum necessary to completely dissolve the CD because the water would eventually need to be evaporated from the samples. These mixtures were placed on aluminum pans and put in a vacuum oven at 50 °C for approximately 18 hours.

Table 1. Amounts of soil, water, and cyclodextrin used to prepare samples.

Soil	Amount (g)	CD used	Amount (g)	DI H_2O (in μL)
Montmorillonite	1.3237	None	0	4000
Montmorillonite	0.2524	Alpha (α)	0.2513	2000
Montmorillonite	0.2509	Beta (β)	0.2502	2000
Montmorillonite	0.2543	Gamma (γ)	0.246	2000
Montmorillonite	0.2493	Maltosyl β	0.2501	2000
Montmorillonite	0.28	Carboxymethyl β	0.253	2000
Montmorillonite	0.2596	Hydroxypropyl β	0.2506	2000
Montmorillonite	0.2581	Amino β	0.1045	2000
Illite	1.0196	None	0	1000
Illite	0.5194	Alpha (α)	0.5248	1000
Illite	0.5197	Beta (β)	0.5169	1000
Illite	0.5202	Gamma (γ)	0.5603	1000
Illite	0.497	Maltosyl β	0.5489	1000
Illite	0.512	Carboxymethyl β	0.5093	1000
Illite	0.5156	Hydroxypropyl β	0.5192	1000
Illite	1.0299	Amino β	0.2525	1000

A Bruker General Area Detector Diffraction System (GADDS) was used to collect images of the various powder samples listed in Table 1. This system utilizes point source x-rays using a copper anode with a K_α wavelength of 1.54178 Å. The samples were exposed to x-rays, and diffraction patterns were collected and analyzed at diffraction angles from $1 - 10$ degrees. A special 0.5 mm brass backstop was machined to collect the x-rays in the $1 - 2$ degree range on the GADDS so the detector would not be directly exposed to the x-rays. These patterns were analyzed using the provided GADDS control software package. Bragg's Equation, shown below in Equation 5 was used to determine the change in the basal spacing:

$$2d \sin \theta = n\lambda \qquad (5)$$

where d is the basal spacing, θ is the diffraction angle, λ is the x-ray wavelength, and n is an integer.

Diffraction patterns of γ-CD and carboxymethyl β-CD individually were gathered to determine if non-absorbed CD could have affected the diffraction patterns of the other eight samples.

4 Results

Electrokinetic Transport

Preliminary EK experiments were performed on uncontaminated kaolinite samples to set upper and lower bounds for the ranges of several operating parameters. In these experiments, uncontaminated kaolinite was mixed with solutions of known conductivities. The resulting samples were packed into 2 in. columns, and solutions of the same conductivity were placed in the anode and cathode chambers of each cell. The samples were then placed under a constant-voltage electric field (100 V) for 24 hours. The resulting difference in height between the solution in the anode and the cathode chamber was measured and plotted as a function of initial solution conductivity. Results are shown in Figure 5 below. It is evident that there exists some optimal solution conductivity for increased electro-osmotic flow. However, this task was beyond the scope of this study so an optimum value was not pursued. Instead, the boundaries for this operating parameter were set between 500 and 1500 ppm dissolved solids in future experiments.
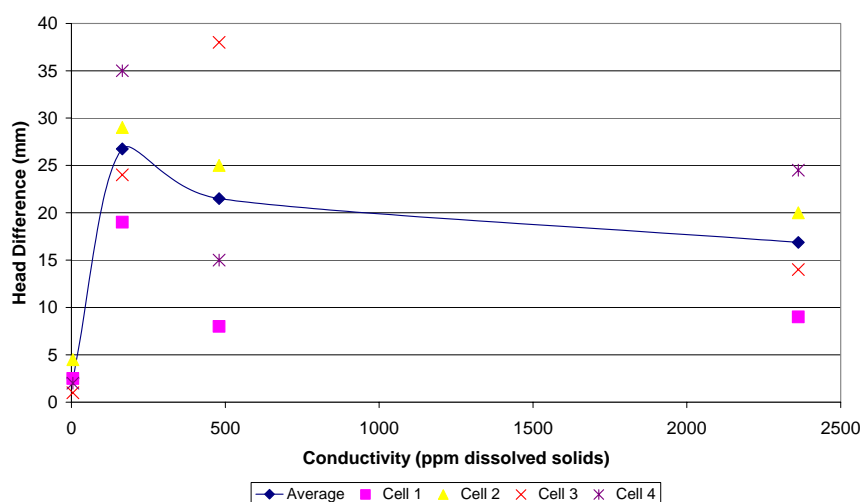

Figure 5. Dependence of electro-osmotic transport on initial solution conductivity.

The purpose of the preliminary experiment was to determine a unit step response of the clay system to an applied electric field. The duration of 24 hours

seems to be a long time scale for such an experiment, but it was necessary to capture the slow physics of the system. Ideally, for this type of experiment, the current flowing through the clay-filled column would have remained approximately constant throughout the duration. However, due to the disparate time scales of soil resistivity change and electro-osmotic flow, this was not the case. The current flowing through the column decreased rapidly with time compared to the timescale for EO flow. This unintended consequence led to the direct verification of the well-know result that the primary force driving EO flow–current density–decreases with time. Some representative results are shown in Figure 6. This phenomenon directly leads to a corresponding decrease in EO flow with time.
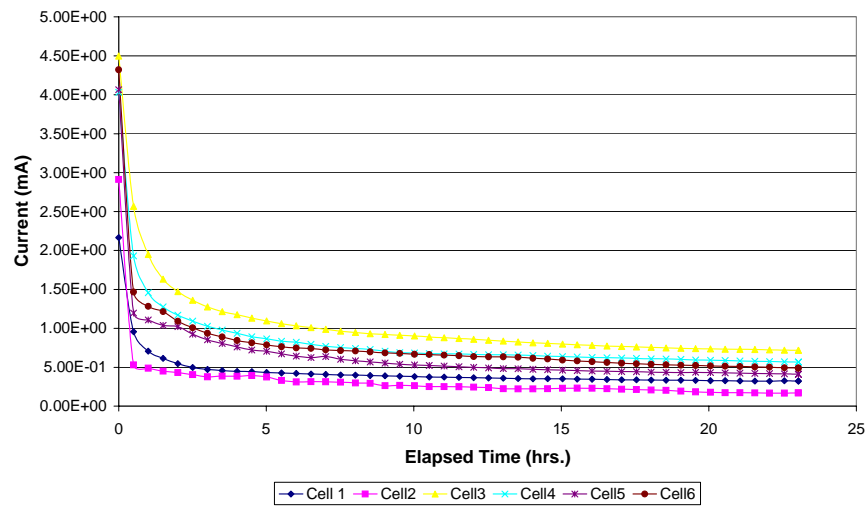
Figure 6. Current as a function of time across six identical kaolinite samples.

The prevailing view in the literature is that this decrease in current and EO flow is due to the migration of an acid front from the anode into the clay medium. The zeta potential of the clay is highly dependent on the pH of the pore solution, with decreasing pH resulting in a lower potential. For sufficiently low values of pH, the zeta potential actually reverses sign, causing a reversed EO flow (47), as shown in Figure 7. While the acidity of the soil adjacent to the anode was not directly tested, pH measurements were taken of the solution in the anode chamber. These data are presented along with the conductivity of the solution in the anode taken upon conclusion of the experiment in Table 2.
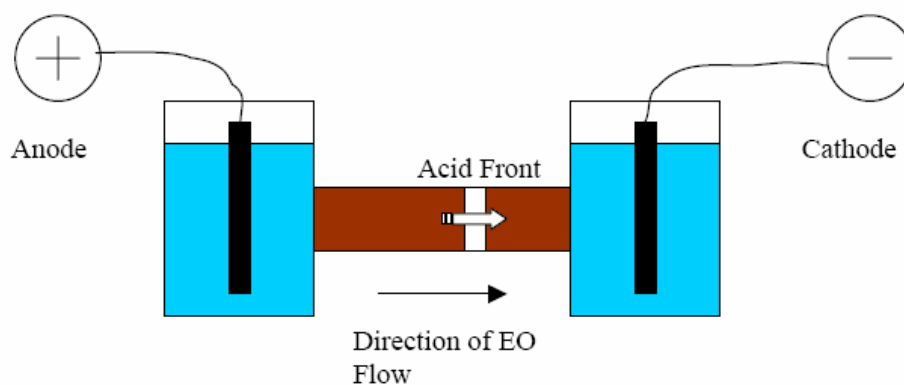
Figure 7. Clay sample potential and EO flow.

**Table 2. Solution pH and conductivity after 24 hours of operation
in anode and cathode chambers.**

Cell	Final Anode pH	Final Anode Conductivity (ppm dissolved solids)	Final Cathode pH	Final Cathode Conductivity (ppm dissolved solids)
1	5	140	8.5	155
2	6	180	8.5	170
3	2.5	465	9	150
4	2.5	385	9	145
5	3	280	9	150
6	2.5	375	9	155

These data indicate that the pH in the anode chamber has become significantly more acidic. Similar experiments were performed for solutions of varying initial conductivity, but the results are not shown here. The magnitude of the difference between anode and cathode pH was even greater for those samples although the increase generally resulted from a marked increase in the pH of the cathode chamber instead of a further decrease in anode pH. It is not hard to imagine, then, that the pore solution within the clay sample near the anode is acidic as well. These results underscore the need for an effective method of neutralizing this pH front.

It was decided that the most effective method of controlling the pH of the soil was to periodically introduce a highly alkaline solution into the anode reservoir. This was accomplished by saturating the anode reservoir with NaOH. The dissociated Na^+ ions would serve as the charge-carrying medium between reservoirs while the OH^- ions would effectively neutralize the H^+ ions produced by electrolysis at the anode, thereby maintaining a neutral to alkaline solution in the anode chamber.

Having determined the EK operating parameters, focus was shifted to answering the question of whether EO flow can transport CDs through a clay matrix. Experiments were designed to answer this question for expansive montmorillonite clay. The parameters determined above were used in conjunction with the EK test procedure described in the previous section. Solutions of 1000 ppm β-CD mixed in tap water were placed in the anode chambers of the test cells while an equal volume of tap water was placed in the cathode chambers. A constant voltage of 25 v was applied across the test cells. Samples from the cathode chamber were taken daily and analyzed for β-CD content. Results are shown in Figure 8.
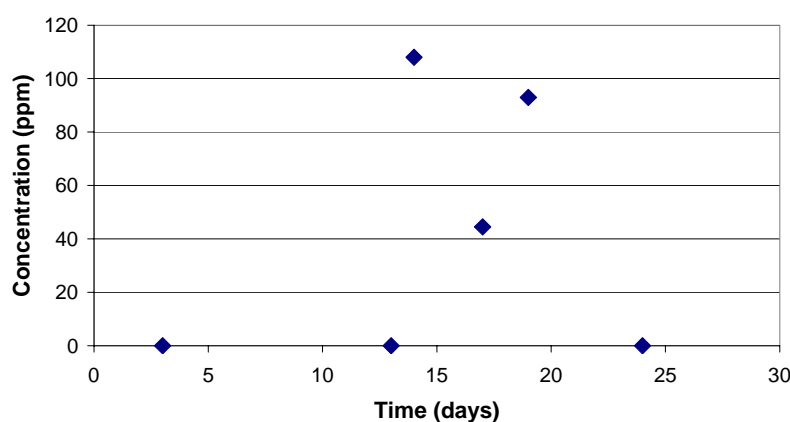
Figure 8. Concentration of β-cd present in cathode chamber as a function of time.

It is clear from this figure that the β-CD can be migrated through expansive clays by electro-osmosis. An interesting note is that Figure 8 clearly shows the concentration of β-CD decreasing with time in the cathode chamber. This occurs after a sharp increase in the concentration of the solution prior to which no CDs were detected. The most likely explanation for this phenomenon is that the CDs are dragged through the matrix with the pore solution at a given rate. The initial concentration spike corresponds to the initial breakthrough of CDs into the chamber. The decrease in concentration seen over time is due to the breakdown of the CD molecules upon interaction with the cathode. This phenomenon was studied more closely, and the details are presented in a later section. This rate of destruction is faster than the net flux of CDs into the cathode chamber, thereby producing the net decrease in concentration observed. It is unclear as to what process controls the net flux of CDs into the cathode chamber. It should be noted that additional CDs are not introduced into the system during the course of the experiment. Only the CDs that were present initially in the anode chamber have the potential to end up in the cathode chamber. This leaves open the possibility that all of the CDs present in the anode chamber had either migrated into the clay or were decomposed at the cathode. Analysis of the solution remaining in the anode chamber was not performed. Determining the ultimate

fate of the CD was not attempted owing to the inability to extract CDs from montmorillonite slurries in batch experiments and the difficulties inherent in identifying the breakdown products of uncharged CDs. Thus it was considered impractical to attempt to perform such a study as part of the present work.

Instead, efforts were focused on determining the complexation behavior of CDs with various contaminants. One representative result is illustrated here. Figure 9 shows the amount of nitrobenzene solubilized by the uncharged cyclo-dextrins: α, β, and γ. These molecules are functionally identical in shape with the exception of interior cavity size, as discussed in Chapter 2. The graph shows the amount of nitrobenzene soluble in water alone (0.03 mM CD added) and the increasing amounts of nitrobenzene solubilized upon addition of the CDs. Better complexation behavior between the nitrobenzene and the CD leads to an in-creased amount in the solution. It is known that the cavity size of the cyclodex-trin molecule relative to the size of the potential guest molecule is a critical fac-tor in whether or not complexation is achieved (42). The results clearly indicate that the most efficient CD for complexation with nitrobenzene is the α-CD.
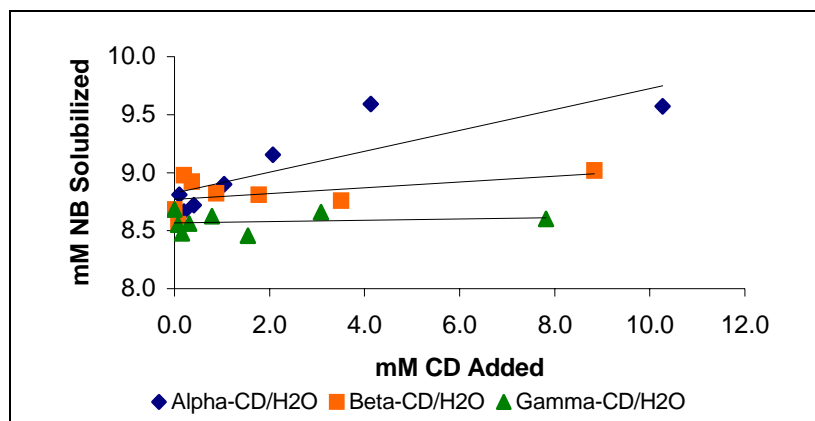
Figure 9. Molar fraction of nitrobenzene solubilized by several different uncharged cyclodextrins.

The next logical question to ask is whether a CD/contaminant complex can be transported via electro-osmosis once it is formed. To answer this question, solu-tions of fully complexed α-CD and nitrobenzene were prepared. The experimen-tal cells were prepared in the same manner as in the previous set of EK experi-ments with the exception that the background solution used was a 1000 ppm NaCl solution. This concentration was chosen as a more controlled parameter with well defined conductivity in an attempt to improve the repeatability of the experiments. For reasons explained in a later section, only montmorillonite clay samples were considered. Samples were taken from the cathode chambers when sufficient electro-osmotic flow had accumulated. In this experiment, the anode chambers were replenished with the α-CD/nitrobenzene complex solution when

necessary. A plot of the concentration of α-CD and nitrobenzene present in the cathode chamber with time is shown in Figure 10.
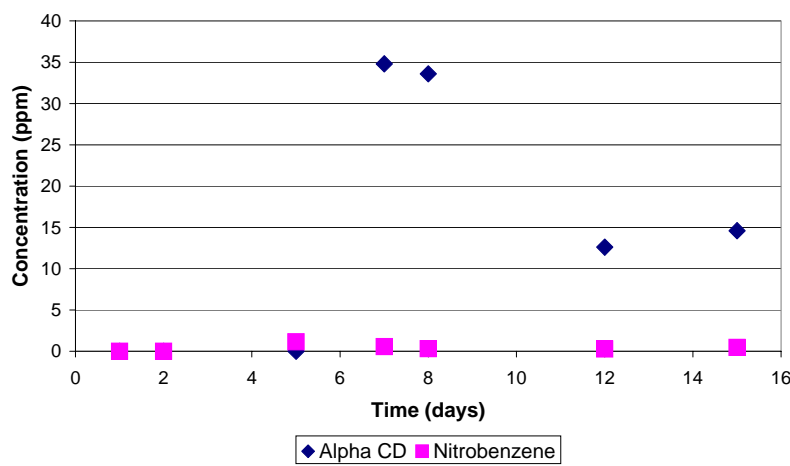
a.

	Concentration (ppm)		
Days	α-CD	Nitrobenzene	Ratio
1	0	0	N/A
2	0	0	N/A
5	0	1.15	0
7	34.8	0.56	62.4
8	33.6	0.31	109.4
12	12.6	0.26	47.9
15	14.6	0.48	30.7

b.

Figure 10. Concentration of α-CD and nitrobenzene in cathode chamber over time for complex transport experiment (a) and raw data and ratio of ppm α-CD to ppm nitrobenzene (b).

In this experiment, the breakthrough time for the α-CD was on the order of 1 week, as compared with 2 weeks for the β-CD experiment shown in Figure 8. This difference may be due in part to the difference in molecular size between the α-CD and the β-CD, but it is more likely that the increased breakthrough time was a result of improved electro-osmosis due to the higher concentration of free Na^+ ions in the background solution. It was observed that very small concentrations of nitrobenzene began to appear in the cathode chamber starting around day 5. CD is probably also present in small concentration but below the method detection limit (~10 ppm). These results are tabulated in Figure 10b along with the ratio of the concentration of α-CD to the concentration of nitrobenzene for each sample. The molar ratio of α-CD to nitrobenzene achieved for this experiment in the initial solution was 1.1:1, which corresponds to a mass ratio of 9.1:1. Theoretically, had the complex been transported intact across the clay matrix, that would be the ratio to appear in the cathode chamber. Such was

not the case here, however. Much more α-CD was transported than nitrobenzene, the reasons for which are unclear. It is possible that the complex reacts at the cathode on a rapid time scale (compared with the time between samples), causing the complexes to separate and the nitrobenzene to degrade more rapidly than the α-CD. It has been established in batch experiments that nitrobenzene degrades very rapidly in the presence of an electric field (see Degradation of CDs and Contaminants, page 34). It is also possible that the complexes break apart within the clay, leaving the nitrobenzene free to preferentially bind to the clay surfaces. More research is necessary in this area to determine the fate of the nitrobenzene. It is very interesting, however, that nitrobenzene is electrokinetically transported through the clay column. Previous studies have not shown EK techniques to be effective for removing nonpolar organic molecules from clay (18, 19, 27, 37, 38). The presence of CD may mitigate the binding mechanism of nitrobenzene within the clay layers. The fact that this process may be possible in a highly expansive clay, whereas previous studies have considered only nonexpansive clays, is highly significant in terms of the potential applicability of this EK technique to a wide variety of soil types with low hydraulic permeability.

While not abandoning the initial concept of using the CD molecule as a solubility-enhancing agent, focus was shifted slightly toward determining the capability of EK to effectively remove nitroaromatic compounds from clayey soils. The next set of experiments directly compared the ability of EK alone and EK with α-CD to remove nitrobenzene from contaminated montmorillonite samples. The experiments were prepared and operated under the same conditions as the previous set of experiments with the following exceptions. The clay samples were contaminated with nitrobenzene according to the method described in a previous section. The solutions introduced into the anode chambers were either 1000 ppm NaCl solution or 1000 ppm α-CD mixed into 1000 ppm NaCl solution, depending on the particular cell. Time profiles of the concentration of nitrobenzene in the cathode chambers are plotted in Figure 11 for three representative test cases. Figure 11a and 11b present data taken from experiments in which the concentrations of the molecules were allowed to accumulate (or degrade) over time. The concentrations given in Figure 11c represent the concentration of nitrobenzene that accumulated in the cathode chamber between sampling times. When a sample was taken, the entire volume of solution in the cathode chamber was removed and replaced with fresh NaCl solution. The high concentration of nitrobenzene present on day 7 reflects the fact that the contaminant had been accumulating in the cathode chamber since the previous measurement on day 4.
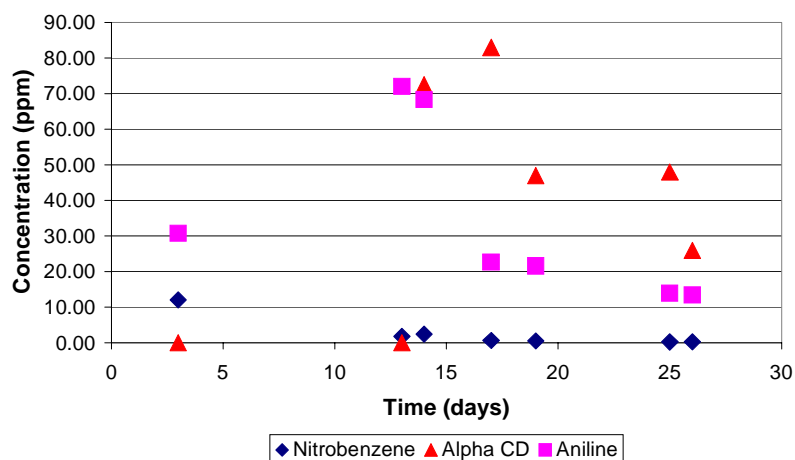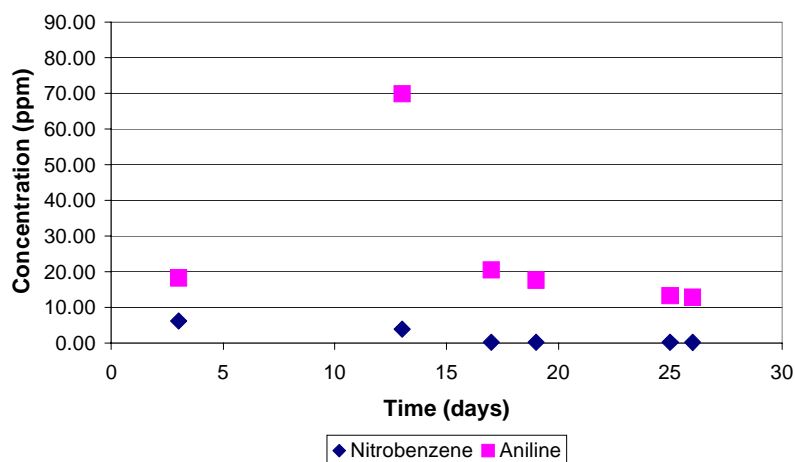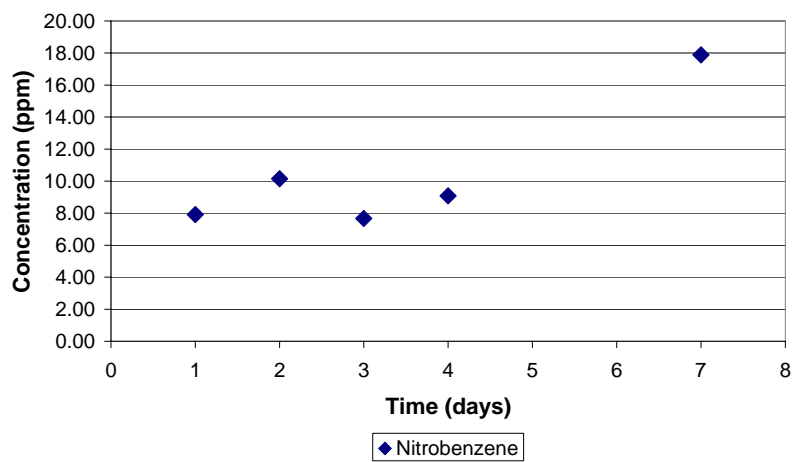
Figure 11. Accumulated concentration of nitrobenzene, aniline, and α-CD in cathode chamber over time (a); accumulated concentration of nitrobenzene and aniline in cathode chamber over time without α-CD added (b); and concentration of nitrobenzene transported to cathode between sampling times without α-CD added (c).

Several conclusions may be drawn from these data. First, Figures 11a and 11b show that the addition of α-CD to the purging solution has no noticeable effect on the amount of nitrobenzene transported into the cathode chamber. Second, similar to CD, nitrobenzene reacts at the cathode to produce reductive byproducts — in this case, aniline. More quantitative results regarding the nitrobenzene degradation process are given under Degradation of CDs and Contaminants, page 34. Third, Figure 11b and 11c clearly show that nitrobenzene can be desorbed and removed from montmorillonite clay by the application of an electric field alone.

It is important to note that these results were obtained using expansive montmorillonite clay as the contaminated soil. It has previously been shown in other studies that α-CD does increase removal efficiencies of various organic molecules from kaolinite, a nonexpansive clay mineral (18). One can also see that in the samples containing α-CD in the purging solution, α-CD appears in the cathode chamber much later than the nitrobenzene (Figure 11a). There are two potential reasons for this. First, if one assumes an approximately uniform distribution of nitrobenzene in the clay matrix, some amount of this molecule is present in the region of the clay nearest to the cathode chamber. Upon initiation of the electric field, this nitrobenzene is mobilized and transported into the cathode chamber. It is clear that this nitrobenzene had to travel a much shorter distance than the α-CD, which was introduced in the anode solution. It should not be surprising, then, that the nitrobenzene would begin to appear in the cathode solutions first. A second possibility is that the transport rate of the α-CD is much slower than that of the nitrobenzene molecule. Based solely on size, it is likely that this is true because the CD molecule is more voluminous than the nitrobenzene molecule. Additionally, any complex that is formed would travel at an even slower rate through the clay, further reducing the likelihood that it would be able to complete its journey through the tortuous interconnected clay matrix. It is doubtful that these effects are mutually exclusive, so it is hypothesized that a combination of these two effects results in more rapid population of the cathode chamber by nitrobenzene molecules than by α-CD molecules. It is apparent that the CD/nitrobenzene complexes interact in some way with the expansive montmorillonite that reduces their effective mobility.

One premise of the argument presented above is that the nitrobenzene molecule is mobilized after only a short period of time following the initiation of the electric field. The basis for this claim lies in the following conjectures. First, it is assumed that there is an abundant source of free sodium ions in the purging solutions. The concentration of sodium ions must exceed the cation exchange capacity of the clay matrix, which implies that the number of free sodium ions ex-

ceeds the number of available interaction sites on the surface of the clay parti-
cles. The second assumption is that it is more energetically favorable to have
sodium ions interacting with the surface of the clay particles than the neutral
nitrobenzene molecules. Finally, the mobility of sodium ions under the influence
of an electric field is much greater than the mobility of both nitrobenzene and
CD molecules. These three assumptions imply that the free sodium ions are dis-
persed throughout the clay matrix almost instantaneously (compared with the
timescale for electro-osmotic flow). There are enough sodium ions to occupy all
unused interaction sites on the clay surface with an excess of ions remaining in
the pore solution. These excess ions will exchange with the nitrobenzene mole-
cules adsorbed to the clay surface. Using these assumptions, it can be seen that
the nitrobenzene molecules will be left free in the pore solution to be transported
by the electro-osmotic flow.

While the above discussion is adequate to explain the ineffectiveness of α-CD in
increasing the removal efficiency of the nitrobenzene, it is doubtful that the ar-
gument is completely physically realistic. In particular, it is unlikely that the
sodium ions will be sufficient to completely liberate all the nitrobenzene mole-
cules from the clay surface. With this thought in mind, it was decided to attempt
to address the shortcomings of the uncharged α-CD used in the previous set of
experiments. By introducing a negatively charged CD into the cathode chamber,
one could transport it into the clay matrix via electromigration in the opposite
direction of the prevailing EO flow. This approach would ensure that the CD
and nitrobenzene would spend at least some time in the proximity of one an-
other, affording the possibility of complex formation. The complex thus formed
would still carry a net negative charge and thus be transported via electromigra-
tion toward the positive anode chamber. An experiment was designed to test
this hypothesis. A solution containing 1000 ppm amino β-CD and 1000 ppm
NaCl was placed in the cathode chambers of the test cells while 1000 ppm NaCl
solution was placed in the anode chambers. Montmorillonite samples contami-
nated with nitrobenzene identical to those in the previous set of experiments
were placed in the cells. A constant voltage was applied across the cells. Sam-
ples were drawn from both the anode and cathode chambers periodically. Time
profiles of the concentration of nitrobenzene in the anode and cathode chambers
of two representative test cells are shown in Figure 12. The nitrobenzene was
transported to both the anode and the cathode chambers in this configuration. It
is unclear from these data as to which direction is the preferred mode of travel
for the nitrobenzene.
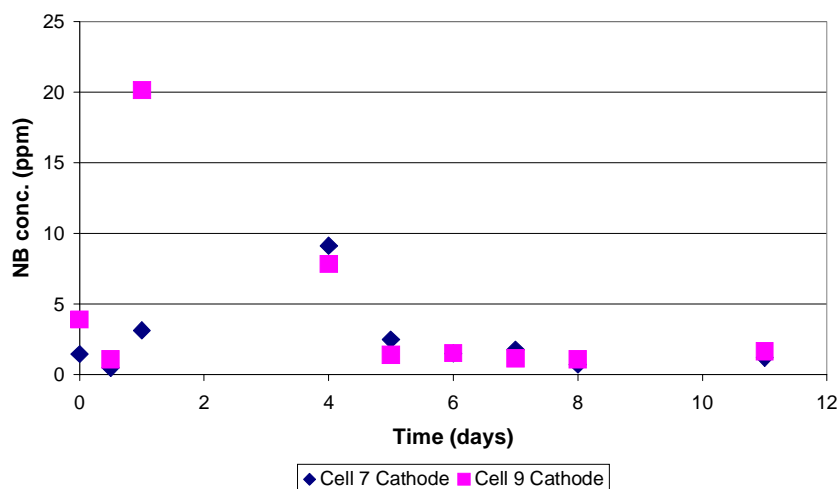
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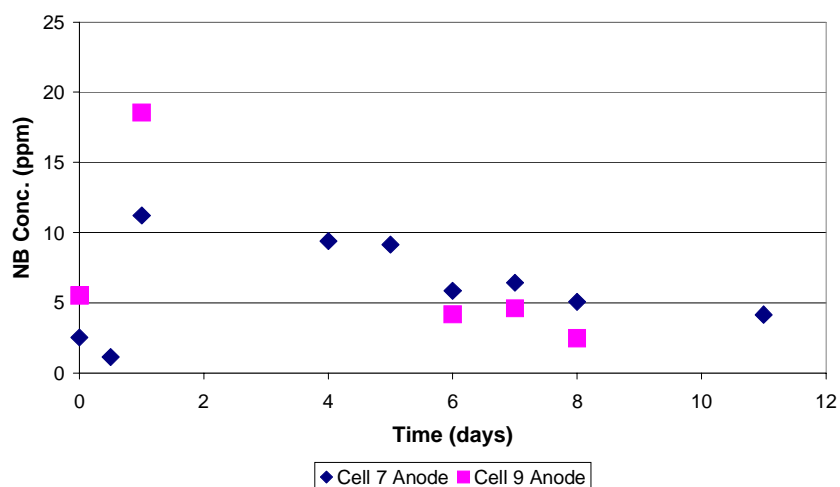
b.

Figure 12. Time profiles of concentration of nitrobenzene in the cathode chambers (a) and the anode chambers (b) of two identical experimental cells with added amino β-CD.

It is noted that nitrobenzene does not bind very strongly to the montmorillonite clay particles. In fact, it has one of the lowest affinities for interaction with clay of any nitroaromatic compound tested, according to data presented in Haderlein et al. (11). Thus, the action of the Na^+ ions can effectively desorb the nitrobenzene from the montmorillonite surface to allow it to be transported via electroosmosis to the cathode chamber. The question arises as to whether the same phenomenon would occur if the clay were contaminated with a molecule having a much higher adsorption constant with montmorillonite. It was found that 2,4-dinitrotoluene (DNT) has an adsorption constant with homo-ionic K^+-montmorillonite that is a factor of 1028 greater than that for nitrobenzene. Although the montmorillonite samples used in this project were natural soils and not homo-ionic, it is expected that 2,4-DNT should have a similar adsorption

constant with the natural montmorillonite. An experiment identical to that de-
scribed in the previous paragraph was performed using 2,4-DNT as the contami-
nant in place of nitrobenzene. As before, the concentration of molecules in both
of the chambers was allowed to accumulate over time. Time profiles of the con-
centration of 2,4-DNT present in both anode and cathode chambers are pre-
sented in Figure 13. These data suggest that electro-osmosis has a much lower
capacity for transporting the contaminant to the cathode chamber, but high con-
centrations are found in the anode chamber.

a.
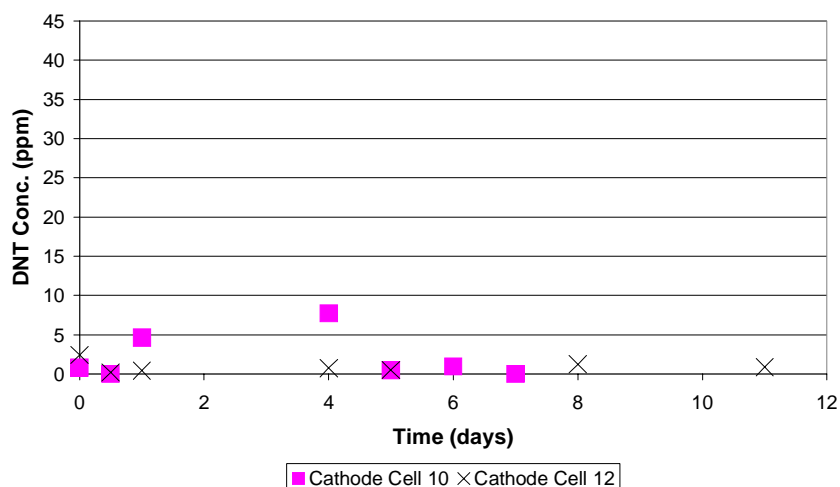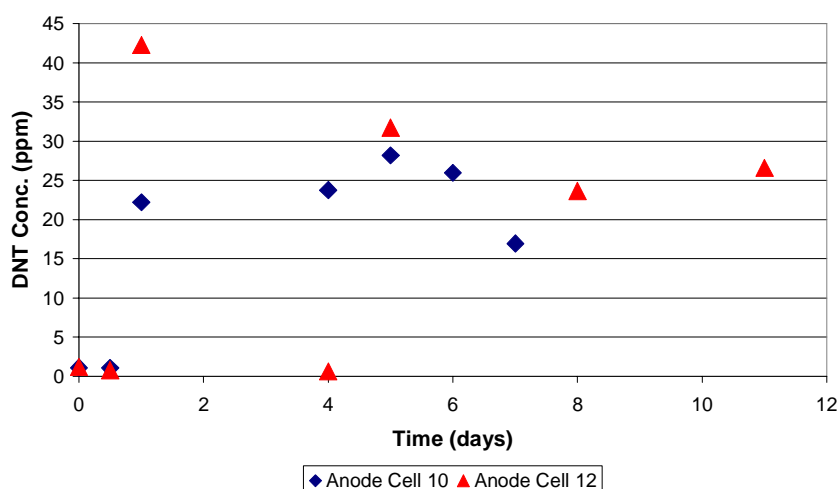

b.

Figure 13. Time profiles of concentration of 2,4-DNT in the cathode chambers (a) and the anode
chambers (b)of two identical experimental cells with added amino β-CD.

This result is very intriguing. The question of what physical process is causing
the 2,4-DNT to move preferentially toward the anode now arises. Nominally it
may seem that the addition of the amino β-CD is performing as hypothesized,

but the possibility cannot be dismissed that the 2,4-DNT is being polarized in some sense and transported via electromigration toward the anode chamber.

The samples drawn from the anode chambers were reanalyzed for amino β-CD, but in all cases the concentrations were below the detection limit of the instrument. Thus it seems that the amino β-CD was either not able to traverse the clay sample or was destroyed immediately upon arrival in the anode chamber. Experiments were conducted to determine whether nitrobenzene and 2,4-DNT were transported to the anode without the assistance of amino β-CD. These experiments were identical in nature to those described above except that the solution added to the cathode chambers did not contain any amino β-CD. After each sample was taken, the entire volume of the anode and cathode chambers was emptied and replaced with fresh NaCl solution. Thus the concentrations shown in Figure 14 represent the amount of the molecule that had accumulated in the electrode chamber between sampling times. The nitrobenzene concentration profiles behave qualitatively in the same manner as those for the experiments conducted with amino β-CD (see Figure 12). There does not seem to be a preferred direction of travel for the molecule. Based on the data presented in Figure 14b, one can argue that the preferred direction of travel for the 2,4-DNT is toward the anode in this case as well, but the amount removed in this case seems to be much lower than that removed in the amino β-CD experiments (see Figure 13b). The data suggest that amino β-CD assists electromigration and removal of tighter bound 2,4-DNT but has very little beneficial effect on the loosely bound nitrobenzene.

For completeness, the same experiment was performed using kaolinite clay samples contaminated with 2,4-DNT. Unlike nitrobenzene, this molecule does sorb well to kaolinite. The concentrations of 2,4-DNT transported out of the clay matrix between samples are shown in Figure 15. It appears that the preferred direction of travel for the 2,4-DNT in this case is toward the cathode instead of the anode, which is opposite of its behavior in montmorillonite. Strongly trapping the 2,4-DNT within the montmorillonite layers inhibits removal by electro-osmosis, but sorbing the 2,4-DNT onto kaolinite surfaces allows some removal by electro-osmosis to occur. This phenomenon may simply be an issue of accessibility. Future experimental work would be needed to understand this transport process.
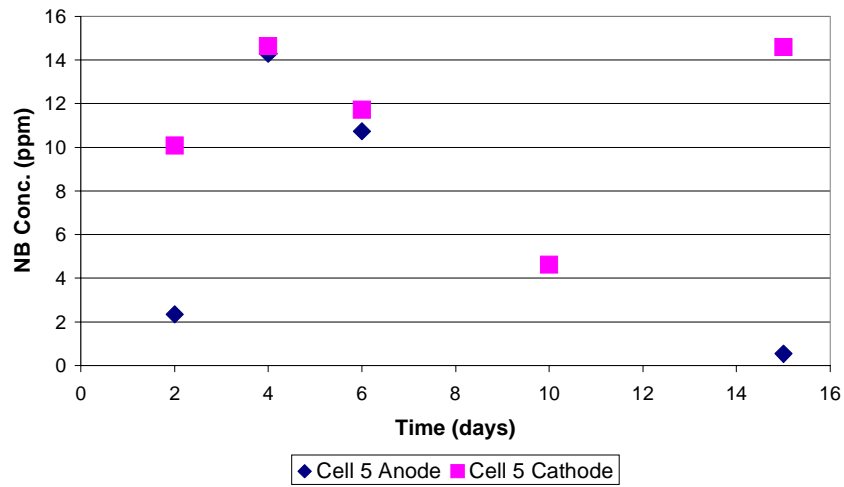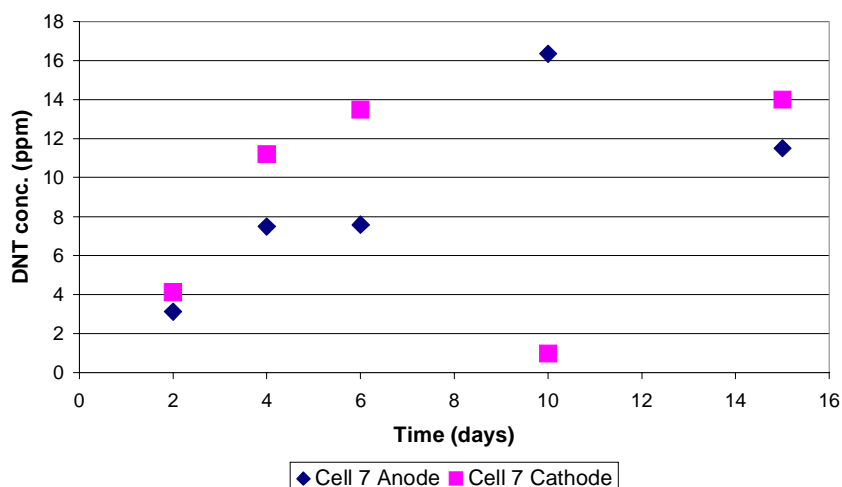
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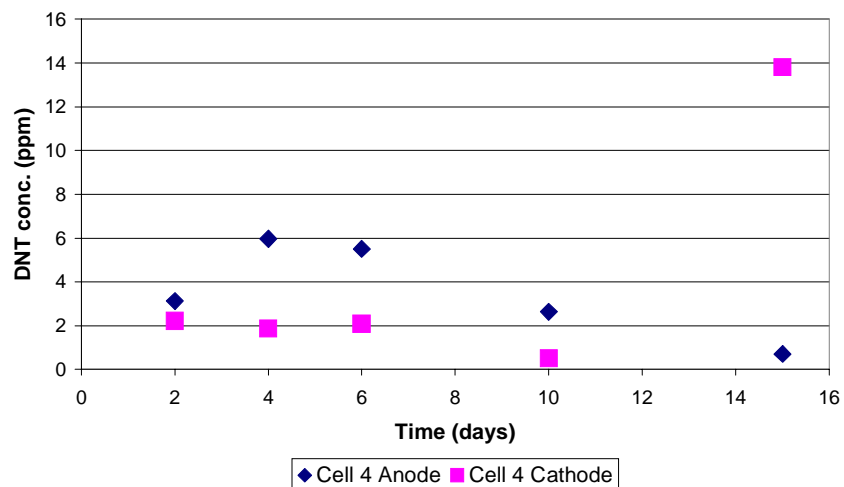
b.

Figure 14. Concentration of nitrobenzene (a) and 2,4-DNT (b) in the anode and cathode chambers of representative montmorillonite test cells, with electrode chamber solution replaced after each sample without added CD.

Figure 15. Concentration of 2,4-DNT in the anode and cathode chambers of a representative kaolinite test cell with electrode chamber solution replaced after each sample.

It became apparent that the most effective method of removing nitrobenzene from montmorillonite was to allow the contaminant to be purged from the soil by the electro-osmotic flow alone. To test the overall efficiency of this method, two batches of montmorillonite were contaminated. The first was contaminated using the method described in Chapter 3 under "Soil Contamination," which ensures that the maximum possible amount of nitrobenzene is sorbed to the montmorillonite. For reference, this value was determined experimentally to be approximately 4.25 mg nitrobenzene per gram of montmorillonite. The second batch was prepared by mixing the fully contaminated montmorillonite with uncontaminated montmorillonite in the proper proportion to achieve a net contamination equal to one-third that of fully contaminated montmorillonite. The total amount of nitrobenzene present in the samples was then determined using EPA Method 8330 (49), as described previously. Both the anode and cathode chambers were filled with 1000 ppm NaCl solutions. Sodium hydroxide was placed in the anode chamber to maintain an alkaline pH throughout the course of the experiment. A constant voltage was applied across all test cells. Cells were taken offline and the amount of nitrobenzene present in the soil samples was once again determined using EPA Method 8330. Figure 16a shows the average percentage of nitrobenzene removed from cells treated for 3, 6, and 12 days. The data points indicate an average over two identical experiments. For comparison, Figure 16b shows the average percentage of nitrobenzene removed from the contaminated montmorillonite in batch experiments using an α-CD solution or an α-CD plus NaCl solution as an extraction solution.
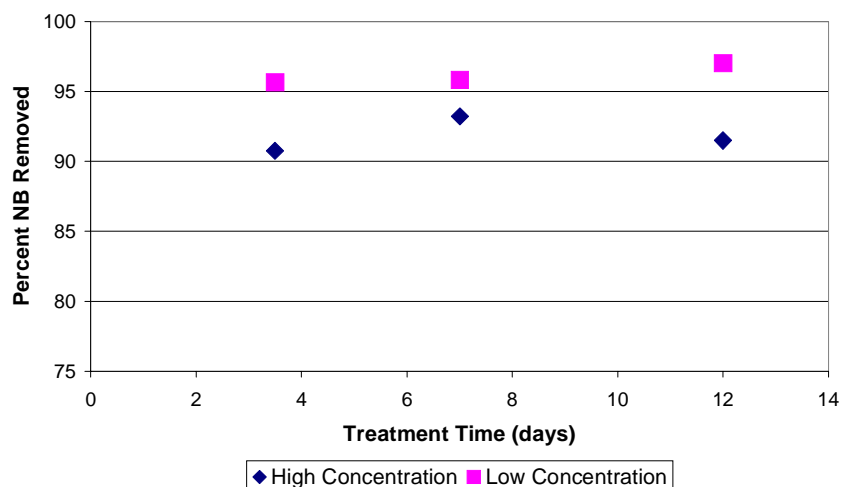
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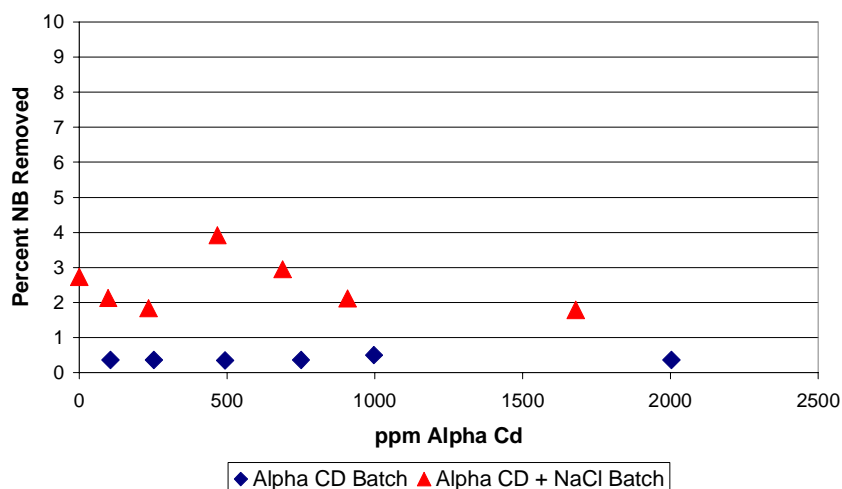
b.

Figure 16. Average percentage of nitrobenzene removed from montmorillonite by electro-osmosis for several different treatment times (a) and average percentage of nitrobenzene removed from montmorillonite in batch experiments (b).

Figure 16a shows that over 90% of the nitrobenzene initially sorbed to the montmorillonite was removed by treatment with electrokinetics for all of the treatment times considered in this study. It is important to point out that in batch experiments represented in Figure 16b, it was possible to remove at most 4% of the nitrobenzene regardless of rinse solution. Thus the ability to remove the model nitroaromatic contaminant nitrobenzene from montmorillonite was greatly enhanced by electrokinetic treatment in a very short time scale. It appears that the treatment reached its maximum effectiveness after just 3 days. Longer treatment times seemingly did little to increase the percentage of nitrobenzene removed.

Degradation of CDs and Contaminants

As noted several times throughout this report, both CD molecules and nitrobenzene molecules can be broken down in the presence of an electric field. The goal of this portion of the research was to quantitatively determine the rate at which a CD or nitrobenzene molecule will be destroyed and what factors significantly affect that rate. To this end, batch experiments were conducted according to the procedure detailed in Chapter 3 under "Electrostatic Degradation".

An experiment to determine the dependence of the degradation rate on the current density was performed. Solutions of 10,000 ppm β-CD were placed in two identical beakers, with twice as much solution being placed in one of them. The extra solution increased the effective area of the immersed electrodes, thereby decreasing the current density since an identical constant current was supplied to both beakers. Solution samples were analyzed to determine any changes in the concentration of CD in the solution over time. The results, presented as the ratio of measured concentrations to initial concentrations, are plotted in Figure 17a.

It is clear from this figure that the applied current density is a very important factor for the rate of CD destruction. An increase in current density by a factor of two resulted in an increase in the rate of destruction by a factor of approximately three for the β-CD sample. It is also important to note that the rate of degradation seems to be almost linear in time. (This result will later be contrasted to experiments performed on a charged CD.)

A similar experiment was conducted using equal volumes of two different CD solutions to determine whether the type of native CD was a factor in determining the overall rate of degradation. A constant current was applied across a 10,000 ppm β-CD solution and a 10,000 ppm α-CD solution. The relative concentration of CD remaining in solution over time is plotted in Figure 17b. One can see that the difference in CD molecules had very little effect on the degradation rate. It should be noted that identification of the breakdown products of the α- and β-CDs was beyond the scope of this study.
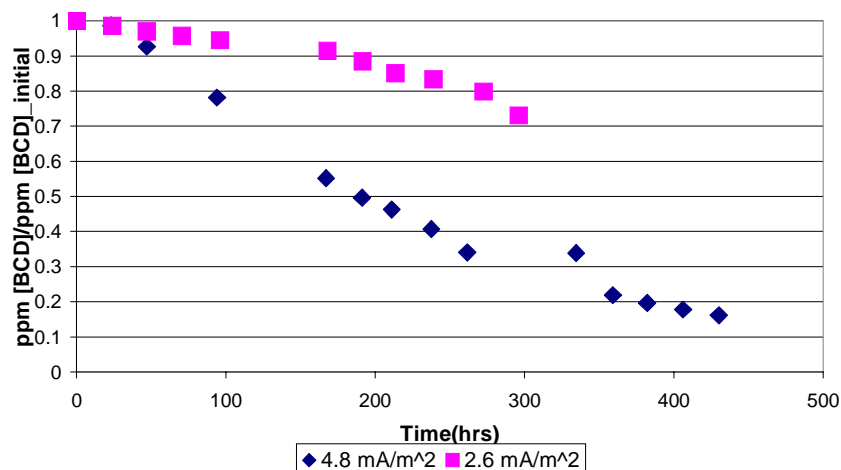
a.
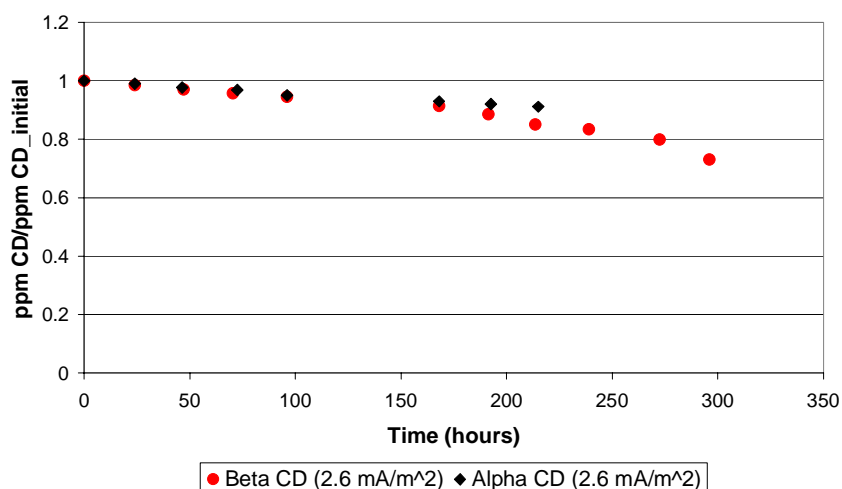
b.

Figure 17. Fraction of CD remaining over time in batch degradation experiments for β-CD under two different current densities (a) and α- and β-CDs under equal current densities (b).

An identical experiment was performed using a 1000 ppm solution of amino β-CD to determine the effect of the charged functional group on the structural stability of the CD. The results of this experiment are shown in Figure 18. Initially, the amino β-CD degraded very rapidly and had seemed to reach a steady-state value, but then after 8 days of operation, the concentration began to degrade again. A physical explanation for this phenomenon is not known at this time nor was it investigated any further in this study due to time and budget constraints. This is an area that appears promising for future work.
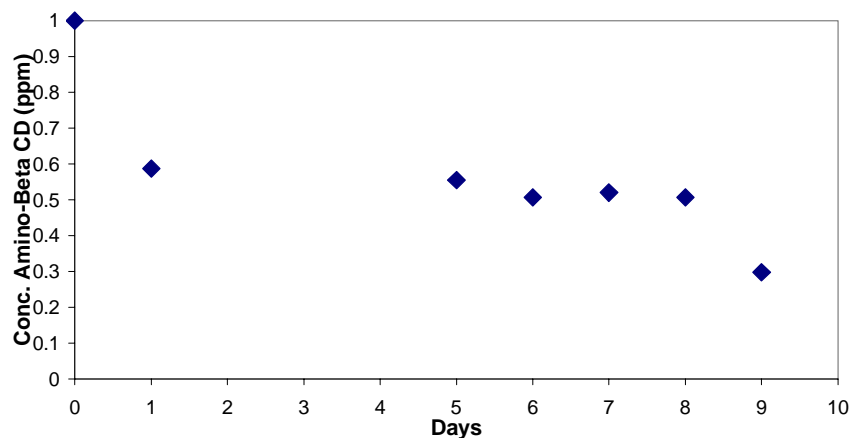
Figure 18. Concentration of amino β-CD remaining in batch degradation experiment over time.

An interesting note to make about this experiment is that, unlike the native CDs, there are appears to be some sort of 'buffer time' for the amino β-CD during which electrostatic degradation stalls. Subject to future verification and additional testing, this effect could be exploited for environmental remediation applications by engineering the molecule to have a specific lifetime after which only environmentally benign breakdown products would remain. Another point of interest is that the breakdown products for the amino β-CD do not include β-CD. Simple loss of amino groups does not appear to be the degradation mechanism.

The behavior of the nitrobenzene molecule under the influence of an electric field was also studied. In a batch experiment similar to those performed with the CDs above, the current density was increased substantially to decrease the time scale of the degradation to the order of hours instead of days in an attempt to decrease any effects caused by uncontrolled experimental variables. Thus, these results must be understood only qualitatively when making a comparison with the CD degradation results. It is interesting to note that much of the degradation occurred almost immediately. In fact, only 40% of the original concentration of nitrobenzene survived the first hour of testing, and the number dropped to close to zero after 5 hours of testing (Figure 19). The rate of decay appears to be pseudo-exponential in contrast to CD degradation. As noted above, nitrobenzene is readily reduced to aniline at the cathode.
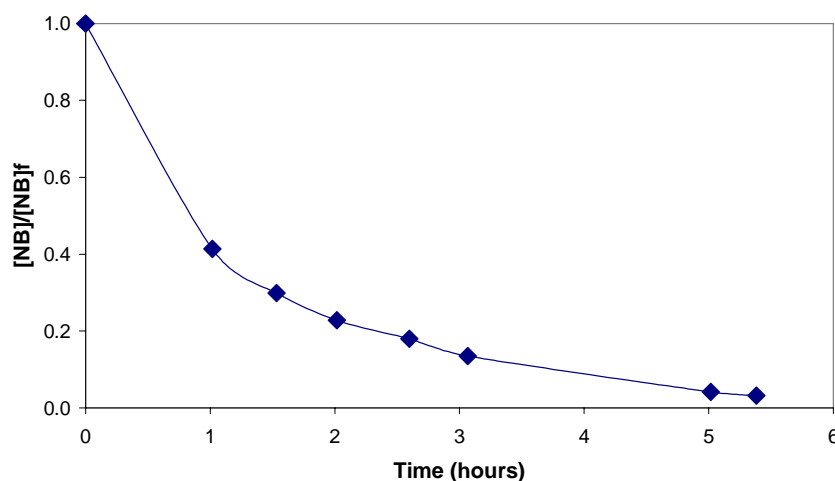
**Figure 19. Concentration of nitrobenzene normalized by initial concentration
remaining in beaker over time in the presence of an electric field.**

X-Ray Diffraction Patterns of Clay-CD Mixtures

Experiments using an x-ray diffraction technique were performed to detect any indications that CD molecules could become incorporated into the interlayer spaces in montmorillonite. Samples of montmorillonite, γ-CD and carboxymethyl β-CD, and several different montmorillonite/CD mixtures were analyzed using this technique, and the results of those experiments are presented in Table 3. The sample of montmorillonite with no CD added has a basal spacing of 12.6 Å. This value is consistent with data presented in MacEwan and Wilson (48) for Na-saturated montmorillonite with a bilayer of hydrated water in the inter-lamellar pore space.   Having established the reliability of the experimental method, it is very likely that the decrease in the d_{001} basal spacing observed for the montmorillonite/CD mixtures is a real phenomenon.

Table 3. Measured basal spacing of montmorillonite and montmorillonite/CD mixtures.

Sample ID	Peak Angle	Basal Spacing (Å)
Montmorillonite	3.51	12.61
Mont. + Alpha	4.04	10.94
Mont. + Beta	3.60	12.29
Mont. + Gamma	3.52	12.56
Mont. + Amino Beta	3.68	12.01
Mont. + Maltosyl Beta	3.78	11.69
Mont. + Hydroxypropyl Beta	3.78	11.69
Mont. + Carboxymethyl Beta	3.54	12.48

Before any attempt is made to explain the possible reasons for such a decrease in the d_{001} spacing, it should be emphasized that the data clearly show that, for all the CDs tested, there is complete adsorption of the CD to the montmorillonite. This result manifests itself in the absence of any resemblance of the diffraction pattern for the CD/montmorillonite mixtures to the diffraction pattern for the pure CDs. This, in combination with the anomalous decrease in the d_{001} upon addition of the CDs, strongly suggests that some type of physical adsorption of the CD to the clay particles has occurred.

Returning to the issue of the decrease in interlayer spacing upon addition of CD molecules into the pore space, it is conjectured that water is excluded from the pore space by the CD molecules upon sample drying. The new basal spacing would then depend on the physical size of the CD independent of relative humidity of the sample-drying environment. The data for the native α-, β-, and γ-CDs support this claim as the d_{001} spacing increases with increasing CD size, suggesting that the CDs form complexes with the montmorillonite such that the glucose ring is oriented at a steep angle to the surface of the clay particles. This phenomenon is seen quite frequently with many long-chain organic molecules. There is considerable debate about the exact nature of the soil-organic molecule bonding mechanism. MacEwan and Wilson (48) list several different possibilities but suggest that van der Waals interactions may be the predominant bonding mechanism for high-molecular-weight organic molecules that are oriented in this nearly perpendicular manner to the clay particle layer arrangement.

The analysis of the modified CDs is much more challenging. Physical size is not the only factor that may determine the interlamellar spacing of the montmorillonite/CD complexes. These modified CDs can carry a net charge of varying strength and polarity. It is highly likely, then, that some other form of bonding mechanism occurs. The cationic CDs (carboxymethyl β-CD) can directly compete with the saturating cations found within the montmorillonite pore structure for available complexation sites on the clay surface. One would suspect that such an electrostatic interaction would tend to be much stronger than the van der Waals interactions that are common for nonpolar organic molecules. This idea would suggest, then, that cationic CDs are bound more tightly to the clay particles than are the native CDs.

The question still remains as to why the interlayer spacing for the samples containing the positively charged carboxymethyl β-CD is larger than that for samples containing the negatively charged β-CDs. This result suggests that the cations present at the clay surface in the interlayer region of the montmorillonite are not readily displaced by the carboxymethyl β-CD and such an electrostatic

reaction as hypothesized above does not occur. Instead, the presence of the CD is in some way shielded from the clay surfaces, and the interlamellar spacing approaches that of pure montmorillonite. The presence of negatively charged ß-CDs, on the other hand, results from a smaller d_{001} spacing than for the uncharged ß-CD. This insight once again indicates the need to revise previous conjecture that the CDs completely exclude water from the interlayer region. It is possible that a surplus of free cations remains near the clay surface and is more strongly attracted to the negative surface groups on the ß-CDs. Thus it could be that this stronger interaction leads to a reduction in the angle of incline of the CD, thereby drawing the clay surfaces closer together. A significant amount of future research in this area would be needed to test these conjectures.

5 Conclusions and Recommendations

Conclusions

This study provided direct evidence that it is possible to remove organic contaminants — in this case nitrobenzene and 2,4-DNT — from expansive montmorillonite clay by electro-osmosis. This type of clay mineral is chemically and physically different from the nonexpansive variety and thus behaves much differently in its capacity to interact with organic molecules, free ions, and electroosmotic flow. It was not clear at the onset of this project whether previous results obtained with nonexpansive soils would hold for the unique case of an expansive soil. Initial batch experiments showed that extractions with various solutions removed very little nitrobenzene from contaminated montmorillonite, while the same process removed nearly all of the nitrobenzene sorbed to kaolinite. This result indicated the inherent difficulties associated with cleaning montmorillonite above and beyond those associated with cleaning kaolinite. In spite of this problem, removal efficiencies of up to 97% were achieved using electroosmosis alone. It is expected that similar removal efficiencies would be generated upon scaling of this technology to the field scale level, so this is a promising area for future work that needs to be addressed. Another critical test of this technology would be needed to verify that similar results can be obtained when the contaminant in question is a nitroaromatic compound that sorbs more strongly to montmorillonite. The 2,4-DNT used in portions of this work would be a likely candidate for such a study along with other contaminants, such as TNT and RDX, that are relevant to Army activities. Additionally, it may be beneficial to test CL20[*] proactively as it represents a potential future environmental contaminant.

The use of native, uncharged cyclodextrins as solubility enhancing agents in combination with electro-osmosis offered little or no improvement over the use of

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[*] CL20: A cyclic nitramine explosive named after Naval Weapons Center China Lake (CL).

electro-osmosis alone in removing nitrobenzene from montmorillonite clay. This result does not align with previous studies showing enhanced removal efficiencies of organic molecules in kaolinite clay. In addition, the ability to transport an intact NB/CD inclusion complex through the clay matrix was not clearly demonstrated. The introduction of negatively charged amino β-CDs into the system through the cathode chambers of the experimental apparatus was able to induce an increased electrokinetic removal of 2,4-DNT. A further set of specialized, more carefully controlled experiments would be needed to reach a definitive conclusion on the benefits of amino β-CD for removal of stronger sorbed nitroaromatic contaminants.

Other results generic to the use of CD molecules in the presence of an electric field were presented. It was found that the structure of the CD molecule is unstable in the presence of an electrical field. Uncharged CDs (α and β) are effectively degraded at a rate dependent upon the current density in the medium in which the CDs are infused. A higher current density results in an increasingly faster rate of degradation while the difference in physical structure and molecular weight between α- and β-CDs has very little effect on the breakdown rate. A charged CD (amino β) is much more unstable in an electric field. Initially, this CD degrades rapidly. Thereafter it seems to survive unscathed for an extended period of time before destruction resumes. By better quantifying this degradation, a kind of designed obsolescence might be engineered for environmental remediation purposes. It also was observed that a CD molecule moves through a clay matrix under the motive EO force at a rate slower than that of smaller organic contaminant molecules that are free in solution.

It also was shown using an x-ray diffraction technique that the CD molecules are physically adsorbed in the interlayer spacing of montmorillonite clay particles. The exact nature and location of the adsorption mechanism is unclear, but it is likely that van der Waals interactions dominate for the uncharged native CD molecules while cationic or anionic interactions probably dominate for the charged CD species. For both of these cases, the most likely orientation for the CD molecule in the interlamellar space is inclined at a steep angle to the clay particle surface. Such a configuration suggests that the d_{001} spacing is dependent on the largest physical dimension of the CD being tested. The implicit assumption behind that conclusion is that the inclination angle depends most strongly on the charge density of the clay particles and the total potential energy of the system rather than on the diameter of the CD molecule. The experimental data support such an argument in that the d_{001} spacing of montmorillonite samples mixed with the native CDs increases with increasing size of the CD molecule. Another open question from this investigation is why the d_{001} spacing actu-

ally decreases due to the addition of the CD molecules. The argument presented here is that the initial spacing is due to a buildup of water layers within the pore space. The added organic CD molecule serves to displace the water from the pore region, thereby causing the to pore size to shrink until it reaches the limit of the physical dimensions of the CD molecule. A significant opportunity for follow-up research exists in that area. A better understanding of the physical mechanisms behind the adsorption of the CD molecules to the clay particles would assist in the development of a process to prevent or reverse this adsorption process.

Recommendations

The ability of electro-osmosis to efficiently clean up contaminated soils should continue to be investigated. The current work could be directly extended to removal of other types of nitroaromatic compounds from montmorillonite on the laboratory scale. Attention also should be given to the more applied aspects of scaling this type of remediation system to a field-scale model.

The use of CDs as solubility-enhancing agents for remediation should still be pursued. Future work in this arena should focus on determining the ability of the native CDs to help remove other organic compounds that adsorb more strongly to the montmorillonite surface. In such cases, the electro-osmotic flow alone may not be sufficient to free the contaminant from the clay surface and transport it out of the clay matrix. By increasing the length of time the CD is in close proximity to the organic contaminant, the likelihood of complex formation should increase accordingly. In such a scenario, the issue of CD durability would need to be addressed more fully and control strategies would need to be developed for this remediation method.

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14. ABSTRACT

Nitroaromatic-based compounds can pose a serious threat to ecosystems and human health. These compounds, which have been used in munitions and pesticides, are present in soil and groundwater at military installations and other sites. The presence of these contaminants in clayey soils poses a difficult and potentially costly remediation problem. The low hydraulic conductivity of these soils prohibits the use of conventional pump-and-treat remediation techniques, and high energy costs make the process of excavating and thermally treating the soil highly inefficient and damaging to the environment. For these reasons, much research has been done to advance the field of electrokinetic remediation as a viable cleanup technique. Although some studies have reported that organic molecules can be removed from clayey soils by electro-osmosis alone using a purging solution, the addition of amendments to the solution has increased removal efficiencies.

The objective of this research was to advance the state of knowledge on a novel technique for cost-effective remediation of nitroaromatic compounds using cyclodextrin molecules as solubilizing agents and electrokinetically transports them through the contaminated zone. The results provided direct evidence that it is possible to remove nitrobenzene and 2,4-DNT from expansive montmorillonite clay using electro-osmosis both with and without cyclodextrin amendments.

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